

# Electrochemical and Infrared Studies of the Reduction of Organic Carbonates

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## INTRODUCTION

Electrolytes typically used in lithium batteries consist of a lithium salt dissolved in an organic solvent, or a mixture of these solvents. The solvents fall into two general classes: ethers or alkyl esters of carbonic acid. Because of lower volatility and higher flash point, the organic carbonates are the preferred solvent class in commercial batteries. Propylene carbonate (PC) has many advantages over other organic carbonates for use in the battery electrolyte, e.g. lower cost and better low temperature performance. Use of PC in Li-ion batteries has, however, been problematic due to co-intercalation of solvent molecules along with  $\text{Li}^+$  ion into the graphite and subsequent exfoliation<sup>1</sup>. The electrolyte commonly used in commercial lithium-ion cells is based on ethylene carbonate (EC), even though these batteries have poorer low temperature performance.<sup>2</sup> Research efforts have, with some success<sup>3,4</sup>, pursued additives to PC to generate a SEI layer that prevents PC co-intercalation. The mechanism of functioning of these additives is, however, still uncertain.

We have performed quantum chemical calculations of the thermodynamic reduction potential of eleven organic molecules at an inert electrode assuming one-electron reduction.<sup>5</sup> Here we report our experimental determinations of the reduction potentials of EC, PC, diethylcarbonate (DEC), dimethylcarbonate (DMC) and vinylene carbonate (VC), and compare them with calculated values. The role of VC as an additive was also investigated and the SEI layer resulting from its reduction characterized by infrared spectroscopy.

## EXPERIMENT

A single compartment glass cell with three electrodes was used for the electrochemical experiments. Lithium metal was used for both counter and reference electrodes. The target solvent specie was dissolved in a THF/0.1M  $\text{LiClO}_4$  supporting electrolyte to a concentration typically of 1 vol % (5 mM in the case of EC). A glassy carbon electrode (1 cm x 1 cm) was used for the FTIR experiments with VC. The composition of the anode was 75% MCMB carbon, 17% SFG-6 graphite, and 8% polyvinylidene difluoride (Kureha C) with a loading of 5.5  $\text{mg}/\text{cm}^2$  applied to both sides of a Cu foil current collector. For the FTIR experiments, the glassy carbon electrode was cycled at 20 mV/s between 0.1 and 2 V, held at the VC reduction potential for five minutes, then brought back to 2 V. The electrode was emersed from the cell at 2 V, and inserted without rinsing into a gastight IR cell fitted with a KBr window. Ex-situ IR microscopy was conducted using a Nicolet Magna 760 spectrometer fitted with a Nic-Plan IR Microscope.

## RESULTS AND DISCUSSION

Infrared reflection absorption (IRRAS) spectroscopy was used to investigate the chemistry of VC reduction. The results are shown in Figure 1. IRRAS spectra from the surface of the glassy carbon electrode held at 1.2 V in THF supporting electrolyte with 5 vol% VC shows new peaks

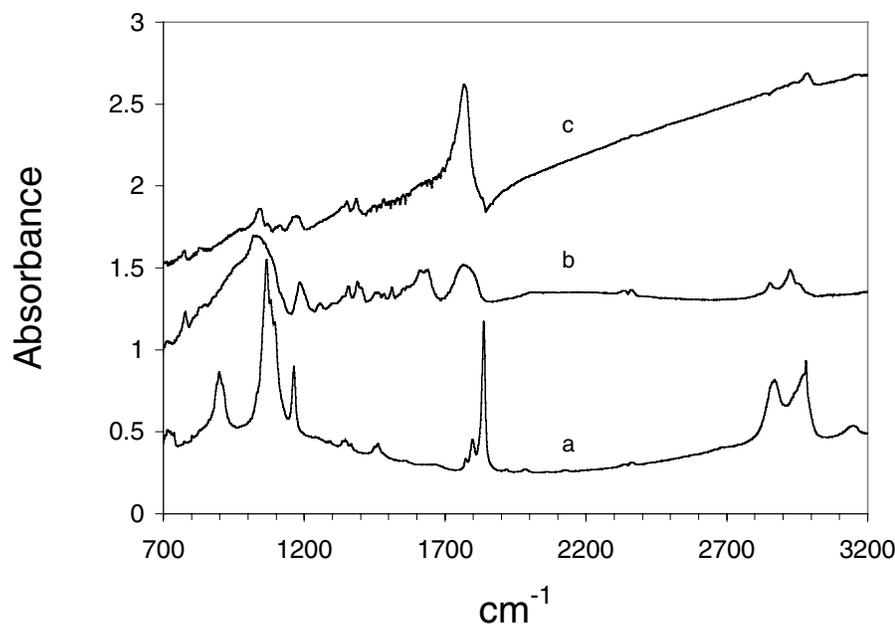


Figure 1. IRRAS of a) VC/THF-LiClO<sub>4</sub> electrolyte before reduction, b) VC/THF-LiClO<sub>4</sub> electrolyte after reduction, and c) glassy carbon electrode surface after reduction in VC/THF-LiClO<sub>4</sub>.

different from the supporting electrolyte, and attributed to VC reduction. The absorption peak at 1640 cm<sup>-1</sup> corresponds to the C=O stretching mode of an alkyl carbonate, and 1620 cm<sup>-1</sup> is assigned to the C=C double bond stretching mode. Note that the C=C double bond stretch is missing in the spectrum of the electrolyte before reduction due to the symmetry of the VC molecule, i.e. there is zero dipole moment. Its appearance in the IR spectra after reduction suggests a ring opening of VC, which creates an unsymmetrical environment about the C=C bond, and causes it to be IR-active. The broad shoulder at 980 cm<sup>-1</sup> is assigned to the out-of-plane C-H bending mode of a methylene (=CH<sub>2</sub>) group<sup>9</sup>. All of these point to lithium vinyl carbonate as one of the reduction products of VC, and a major component in the organic layer of the SEI. The suggested reduction mechanism of VC reduction, shown in the Scheme, involves the formation of a bond-broken radical anion (5B), which undergoes a hydrogen abstraction to produce the unsaturated lithium alkylcarbonate anion (5C). The spectrum for the bulk electrolyte after reduction shows similar features to that from the electrode, which suggests that the lithium vinyl carbonate salt is partly soluble in the electrolyte.

IRRAS spectra were also obtained from the composite carbon electrode cycled in PC electrolyte with and without the 5 % VC additive (not shown). Although the quality of the spectrum from this porous electrode was not equal to those from the glassy carbon, the IR features assigned to VC reduction products were observed. This suggests that VC reduction at potentials above 1.2 V, before Li<sup>+</sup> ion intercalation, forms a protective layer that prevents PC co-intercalation and graphite exfoliation. Although the other carbonates EC, DEC and DMC also have reduction potentials positive of Li<sup>+</sup> ion intercalation, use of EC/DEC/DMC as *additives* to PC, i.e. at the concentrations of a few vol %, does not produce the same protection against graphite exfoliation as VC. The difference would appear to be due to the unique morphology and/or microstructure of the reduction layer formed by VC reduction.

## SUMMARY

The electrochemical reduction of five organic carbonates, EC, PC, DEC, DMC and VC were studied via cyclic voltammetry at a Au electrode. More detailed studies of the chemistry of VC reduction were carried out using IRRAS at a glassy carbon electrode. The measured reduction potentials for EC, DEC and PC were consistent with thermodynamic values calculated using density functional theory (DFT) assuming one-electron reduction to the radical anion. The experimental values for VC and DMC were, however, much more positive than the calculated values, which we attribute to different reaction pathways. The role of VC as an additive in a PC-based electrolyte was investigated. We confirmed stable cycling of a commercial lithium-ion battery carbon anode in a PC-based electrolyte with 5 mol % VC added. A surface layer indicative of preferential reduction of VC in the PC-based electrolyte was observed by IRRAS with both a glassy carbon and composite carbon electrode. The preferential reduction of VC and the SEI layer formation therefrom appears to inhibit PC co-intercalation and subsequent graphite exfoliation.

## REFERENCES

- (1) Besenhard, J. O.; Fritz, H. P. *J. Electrochem. Soc.*, **53**, 329 (1974).
- (2) Winter, M.; Besenhard, J. O.; Spahr, M. E.; Novak, P. *Adv. Mater.*, **10**, 725 (1998).
- (3) Wang, C.; Nakamura, H.; Komatsu, H.; Yoshio, M.; Yoshitake, H. *J. Power Sources*, **74**, 142 (1998).
- (4) Jehoulet, C.; Biensan, P.; Bodet, J. M.; Broussely, M.; Moteau, C.; Tessier-Lescouret, C. *ECS Meeting Abstracts*, vol. MA 97-2, 135 (1997).
- (5) Zhang, X.; Pugh, J. K.; Ross, P. N. In *J. Electrochem. Soc.*, (2000).
- (6) Aurbach, D.; Daroux, M.; Faguy, P.; Yeager, E. *J. Electroanal. Chem.*, **297**, 225 (1991).
- (7) Campbell, S. A.; Bowes, C.; McMillan, R. S. *J. Electroanal. Chem.*, **284**, 195 (1990).
- (8) Pletcher, D.; Rohan, J. F.; Ritchie, A. G. *Electrochim. Acta* **39**, 1369 (1994).
- (9) Smith, B. *Infrared spectral interpretation*; CRC Press LLC:, (1998).

This research was funded by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Advanced Automotive Technologies, U. S. Department of Energy, under contract DE-AC03-76SF00098.

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